PB-234 151

COLLABORATIVE STUDY OF METHOD FOR THE DETERMINATION OF PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES (MUNICIPAL INCINERATORS)

Henry F. Hamil, et al

Southwest Research Institute

Prepared for:

Environmental Protection Agency

1 July 1974

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-650/4-74-022	2.
3.	PB 234 151
4. TITLE AND SUBTITLE: Collaborative Study of Method for the Determination of Particulate Matter Emissions from Stationary Sources (Municipal Incinerators).	5. REPORT DATE: July 1, 1974
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Henry F. Hamil and Richard E. Thomas	8. PERFORMING ORGANIZATION REPORT NO.: SwRI 01-3462-002
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Southwest Research Institute, 8500 Culebra Road, San Antonio, Texas 78228	10. PROGRAM ELEMENT NO.: 1HA327 (ROAP 26AAG)
	11. CONTRACT/GRANT NO.: 68-02-0626
12. SPONSORING AGENCY NAME AND ADDRESS: Environmental Protection Agency, NERC, Quality Assurance & Environmental Monitoring Laboratory, Methods Standardization Branch, Research Triangle Park, N. C. 27711	13. TYPE OF REPORT AND PERIOD COVERED: Final Report
	14. SPONSORING AGENCY CODE
15. SUPPLEMENTARY NOTES	

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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18. DISTRIBUTION STATEMENT: Unlimited	19. SECURITY CLASS (This Report): Unclassified	21. NO. OF PAGES: 37
	20. SECURITY CLASS (This page): Unclassified	22. PRICE: 5.00 - 1.45

EPA Form 2220-1 (9-73)

SOUTHWEST RESEARCH INSTITUTE
Post Office Drawer 28510, 8500 Culebra Road
San Antonio, Texas 78228

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by
Henry F. Hamil
Richard E. Thomas

EPA Contract No. 68-02-0626
SwRI Project No. 01-3462-002

Prepared for
Methods Standardization Branch
Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center
Environmental Protection Agency
Research Triangle Park, N. C. 27711

Attn: M. Rodney Midgett, Research Chemist
Section Chief, Stationary Source Methods Section

Approved:

John T. Goodwin

John T. Goodwin
Director
Department of Chemistry
and Chemical Engineering

SUMMARY AND CONCLUSIONS

This report presents the results obtained from a collaborative test of Method 5, a test procedure promulgated by the Environmental Protection Agency for the determination of particulate emission levels from stationary sources. Method 5 specifies that particulate matter be withdrawn isokinetically from the source and its weight be determined gravimetrically after removal of uncombined water.

The test was conducted at a municipal incinerator using four collaborative teams. A total of 12 runs were made over a two week period, and 47 individual concentration determinations made by the four collaborators. From these, the values which conformed to the standards of 60 scf of gas collected and ±10% of isokinetic sampling were used in the analysis. The resultant working sample was 11 runs and a total of 32 individual observations. These were submitted to statistical analysis to obtain precision estimates for Method 5.

The precision is expressed in terms of within-laboratory, between-laboratory and laboratory bias components. For purposes of statistical treatment, the determinations are grouped into blocks. Two separate furnace trains were used at the incinerator, the No. 1 unit during the first week of testing, and the No. 2 during the second week. The values obtained from each stack were grouped as a block for this test. The statistical analysis is based on the assumption that the true emission concentration remains essentially constant over the course of each week's runs. No independent method for determining the concentration was available during the test to substantiate this assumption, but a preliminary statistical test on the determinations detected no significant differences among the runs that would indicate a changing mean value over the test period.

The precision components are estimated in terms of standard deviations, which are shown to be proportional to the mean of the Method 5 determinations, δ, and can be summarized as follows:

(a) Within-laboratory: The estimated within-laboratory standard deviation is 25.3% of δ and has 24 degrees of freedom associated with it.

(b) Between-laboratory: The estimated between-laboratory standard deviation is 38.7% of δ, with 3 degrees of freedom.

(c) Laboratory bias: From the above, we can estimate a laboratory bias standard deviation of 29.3% of δ.

The above precision estimates reflect not only operator variability, but, to an extent, source variability which cannot be separated from these terms. Since the results summarized above were obtained from a single test, further testing would, of course, be necessary to obtain conclusive results.

Recommendations are made for the improvement of the precision of Method 5, and considerations given for the use of the method in field testing.

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I. INTRODUCTION

This report describes the work performed and results obtained on Southwest Research Institute Project No. 01-3462-002, Contract No. 68-02-0626, which includes collaborative testing of Method 5 for particulate emissions as given in "Standards of Performance for New Stationary Sources."[1]*

This report describes the collaborative testing of Method 5 at a municipal incinerator, the statistical analysis of the data from the collaborative tests, and the conclusions and recommendations based on the analysis of the data.

*Superscript numbers in parentheses refer to the List of References at the end of this report.

II. COLLABORATIVE TESTING OF METHOD 5

A. Collaborative Test Site

Arrangements were made for collaborative testing of Method 5 at the Holmes Road Incinerator of the Division of Solid Waste Management, Department of Public Works, City of Houston, Texas. Facilities were installed to provide for simultaneous sampling by four collaborators, each collaborative team working on separate ports on a platform on the stack.

The incinerator was visited in November, 1972, to inspect the facilities and conduct preliminary sampling to determine site suitability. At that time, details of site preparation, including addition of platform extensions and additional sampling ports were made. Site modifications were completed in May, 1973, and another site visit was made to assure suitability for collaborative testing.

The 5-yr old facility consists of two parallel furnace trains, with a capacity of 400 tons of refuse per furnace per day. The furnaces are a triple grate continuous feed design. Refuse is transferred from the storage bins to the furnace-charging hoppers by two traveling bridge cranes.

From the charging hoppers, the refuse feeds continuously through water-cooled chutes onto traveling grate stokers in the furnaces. When the residue reaches the end of the combustion grate, it drops through a chute to either of two ash conveyers. The residue is quenched and conveyed to rotating screen separators, which discharge into loading-out hoppers for trucking to the disposal area adjacent to the incinerator plant.

Gases leaving the furnaces are cooled in water spray chambers and then enter the flue gas scrubbers to remove the fly ash. The gases then pass through the induced draft fans and out the stacks. A flow diagram of one of the incinerator units is shown in Figure 1.

Four sampling ports were available on both the Number 1 (east) and Number 2 (west) units. The sample ports were at 90 deg to each other and were offset 6 in. vertically from port to port to avoid probe interference. Access to the sample ports was from a 360-deg platform around the stacks, which were 6.5 ft inside diameter and 148 ft high. The sample ports were 102 ft above grade and 57 ft (8.8 diameters) above the nearest upstream flow disturbance. This allowed the use of 12 traverse points, 6 on each diameter traverse. Sample port layout is shown in Figure 2, and a velocity profile is shown in Figure 3. The velocity profiles were obtained by averaging the velocities obtained at each traverse point by two laboratories on all velocity traverses. A view of the test site and Number 1 stack is in Figure 4.

Pertinent information concerning stack dimensions, sample port location with respect to flow disturbance, and traverse point locations is tabulated in Table 1.

Traversing for the test itself was accomplished as follows (see diagram p. 6): Sampling teams at ports A and B began sampling at points 1 and 1′, respectively. After ten minutes, the team at port A moved to point 2, and the team at port C began sampling at point 1. Simultaneously, the team at port B moved to point 2′ and the team at port D moved to point 1′ and began sampling. This pattern was followed until the diameter traverse was completed (it should be noted that the sampling period of the teams at ports A and B was displaced in time by ten minutes from that of the teams at ports C and D, the assumption being that stack conditions were sufficiently constant to justify this displacement in time. This displacement in time was necessary to avoid interference from two probes sampling the same traverse point simultaneously). Each team then moved its sampling unit to the port on its right (as one faces the stack), and the traversing procedure was repeated. These two diameter traverses then constituted a run. Port heights were varied (see Figure 2) so that interference of the probes was prevented.

The first week of the test was conducted on the Number 1 unit. Failure of the moving grates on that unit necessitated testing on the Number 2 unit during the second week of the test.

1. Tipping Dock
2. Storage Bin
3. Bridge Crane
4. Refuse Feed Hopper
5. Water Cooled Chute
6. Drying Stoker
7. Ignition Stoker
8. Combustion Stoker
9. Secondary Chamber
10. Flue Gas Scrubber
11. Stack
12. Sampling Platform
13. Bypass Stack
14. Forced Draft Fan
15. Overfire Air Fan
16. Induced Draft Fan
17. Residue Chute
18. Residue Conveyors
19. Water Treatment Bldg.

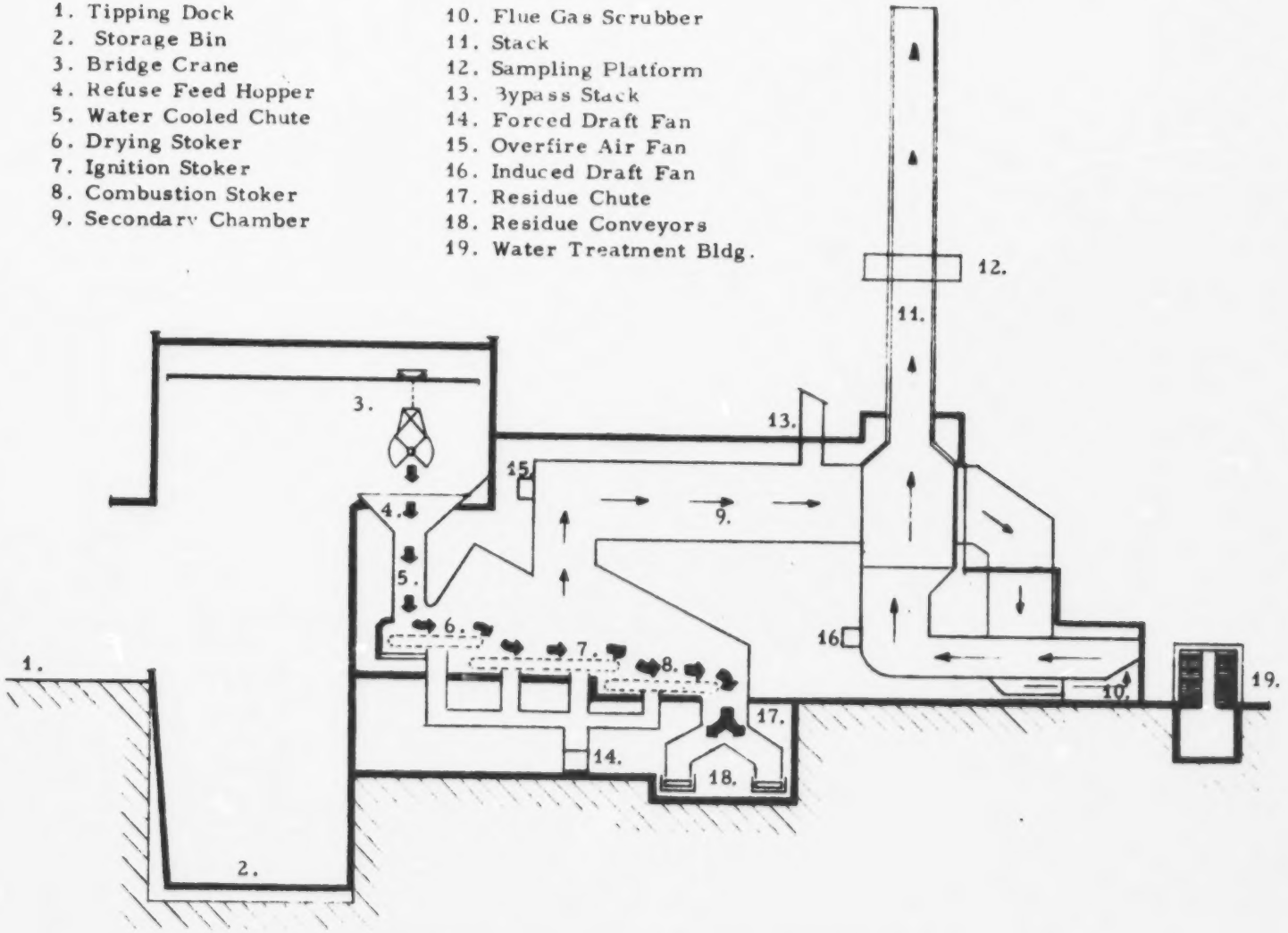


FIGURE 1. FLOW DIAGRAM OF HOLMES ROAD INCINERATOR PLANT

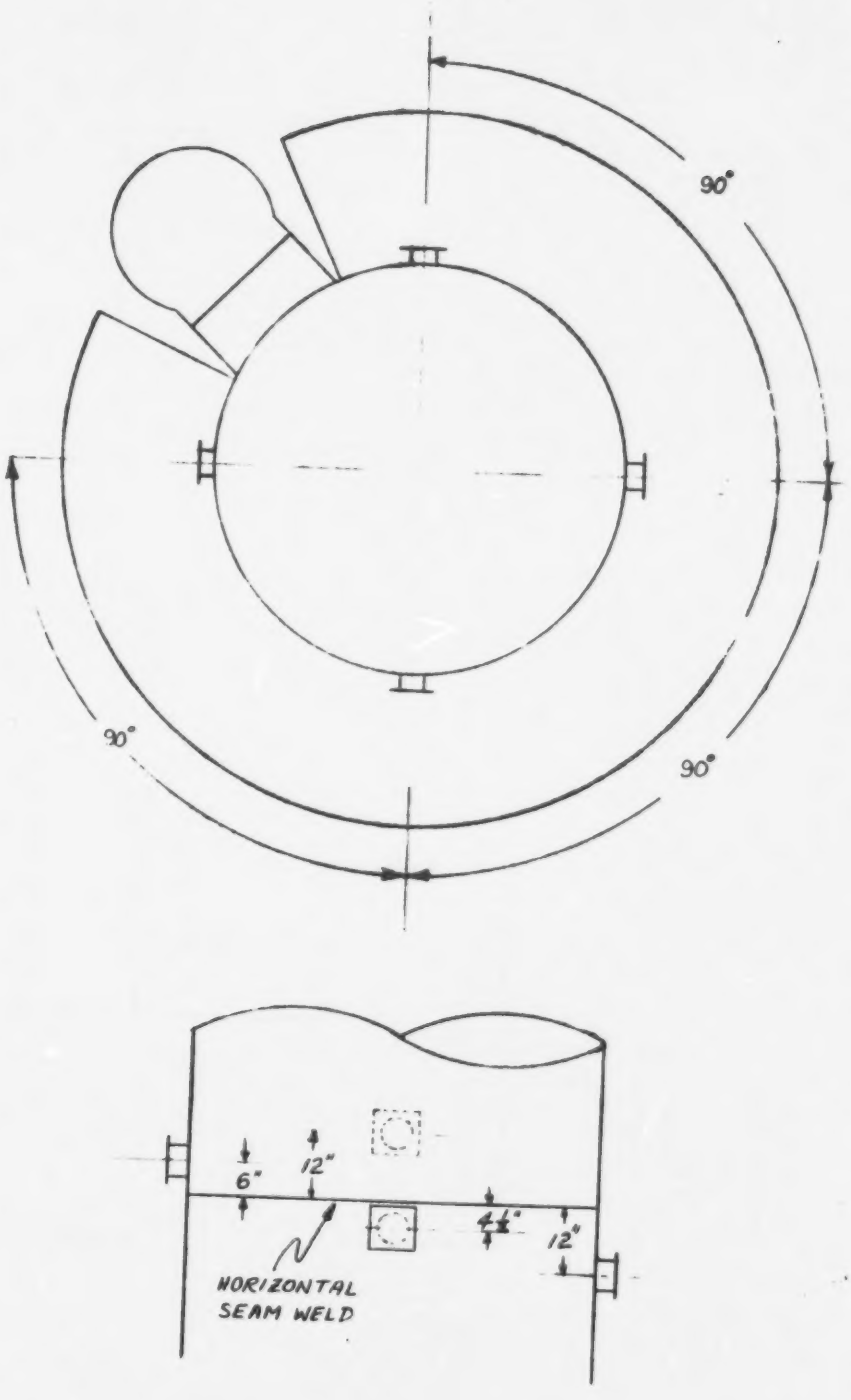
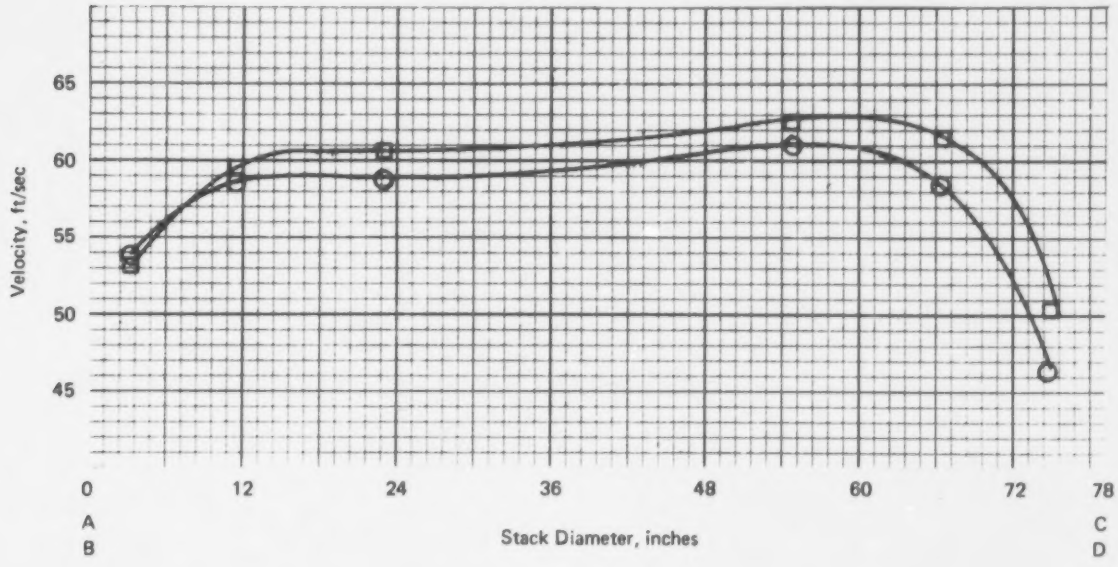
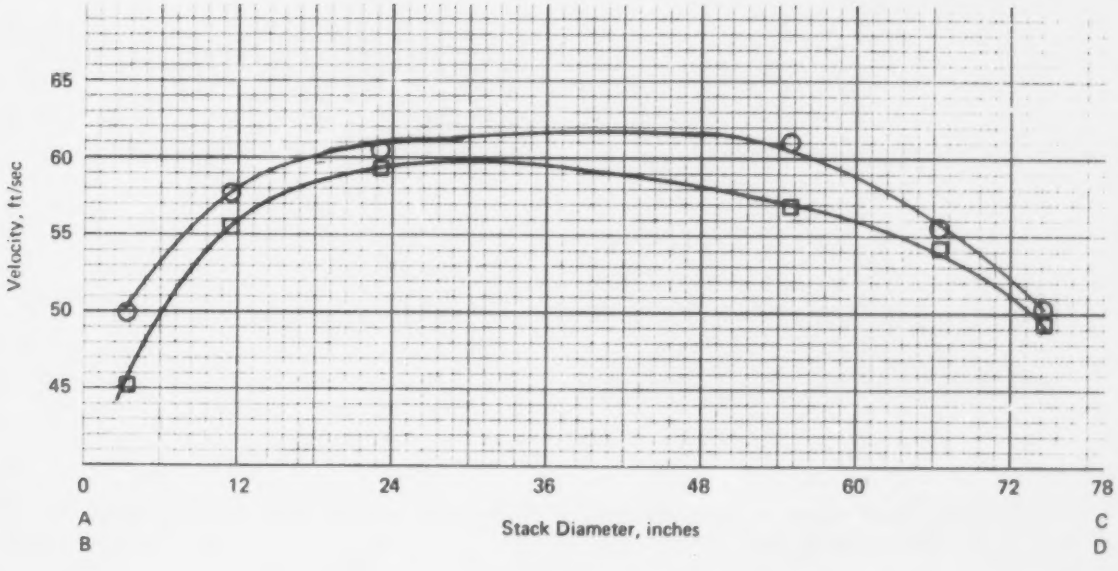


FIGURE 2. SAMPLING PORT CONFIGURATION



Profile, East Stack



Profile, West Stack

□ Axis through ports A, C
○ Axis through ports B, D

FIGURE 3. AVERAGE VELOCITY PROFILES

TABLE 1. TEST SITE DATA

Inside stack diameter:	78 inches
Distance of sampling site from downstream disturbance:	8.8 diameters
Distance of sampling site from upstream disturbance:	>2 diameters
Number of traverse points on a diameter:	6
Sampling time at each traverse point:	10 minutes

Traverse Point	Distance from outside wall to traverse point, inches:
1	3.3/8
2	11-1/2
3	23
4	55
5	66-1/2
6	74-5/8

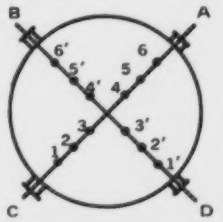


FIGURE 4. HOLMES ROAD INCINERATOR TEST SITE

B. Collaborators

The collaborators for the Holmes Road Incinerator test were Mr. Mike Taylor and Mr. Rick Hohmann of Southwest Research Institute, Houston Laboratory, Houston, Texas; Mr. Charles Rodriguez and Mr. Ron Hawkins of Southwest Research Institute, San Antonio Laboratory, San Antonio, Texas; Mr. Quirino Wong, Mr. Randy Creighton, and Mr. Steve Byrd, City of Houston, Department of Public Health; Mr. John Key, Mr. James Draper, Mr. Tom McMickle, Mr. Tom Palmer, Mr. Michael Lee, and Mr. Charles Goerner, Air Pollution Control Services, Texas State Department of Health.*

Collaborative tests were conducted under the general supervision of Mr. Nollie Swynnerton of Southwest Research Institute. Mr. Swynnerton had the overall responsibility for assuring that the test was conducted in accordance with the collaborative test plan, and that all collaborators adhered to Method 5 as written in the *Federal Register* [1]. Collaborators for the test were selected by Dr. Henry Hamil of Southwest Research Institute.

In Figures 5 and 6, members of the collaborative teams are shown in the operation of impinger trains and a control console during one of the test runs.

C. Philosophy of Collaborative Testing

The concept of collaborative testing followed in the tests discussed in this report involves conducting the test in such a manner as to simulate "real world" testing as closely as possible. "Real world" testing implies that the results obtained during the test by each collaborator would be the same results obtainable if he were sampling alone, without outside supervision and without any additional information from outside sources, i.e., test supervisor or other collaborators.

*Throughout the remainder of this report, the collaborative laboratories are referenced by randomly assigned code numbers as Lab 101, Lab 102, Lab 103, and Lab 104. These code numbers do not correspond to the above ordered listing of collaborators.

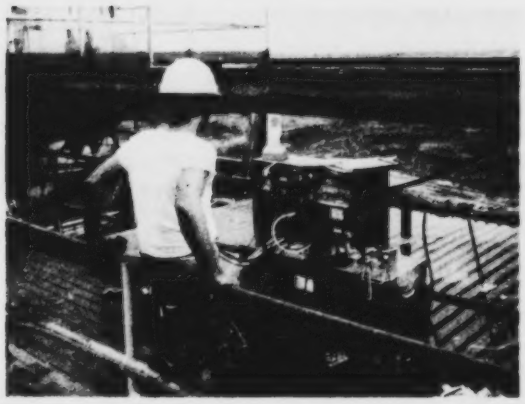


FIGURE 5. CONTROL CONSOLE OPERATION

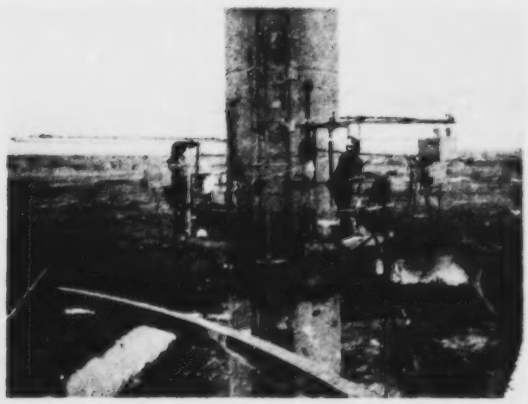


FIGURE 6. IMPINGER TRAIN OPERATION

The function of the test supervisor in such a testing scheme is primarily to see that the method is adhered to as written and that no individual innovations are incorporated into the method by any collaborator. During the test program, the test supervisor observed the collaborators during sampling and sample recovery. If random experimental errors were observed, such as mismeasurement of volume of impinger solution, improper rinsing of probe, etc., no interference was made by the test supervisor. Since such random errors will occur in the everyday use of this method in the field, unduly restrictive supervision of the collaborative test would bias the method with respect to the field test results which will be obtained when the method is put into general usage. However, if gross deviations were observed of such magnitude as to make it clear that the collaborator was not following the method as written, the deviations would be pointed out to the collaborator and corrected by the test supervisor.

While most of the instructions in the *Federal Register* are quite explicit, some areas are subject to interpretation. Where this was the case, the individual collaborators were allowed to exercise their professional judgement as to the interpretation of the instructions.

The overall basis for this so-called "real-world" concept of collaborative testing is to evaluate the subject method in such a manner as to reflect the reliability and precision that would be expected of the method in field testing.

III. STATISTICAL DESIGN AND ANALYSIS

A. Statistical Terminology

To facilitate the understanding of this report and the utilization of its findings, this section explains the statistical terms used in this report. The procedures for obtaining estimates of the pertinent values are developed and justified in the subsequent sections.

We say that an *estimator, $\hat{\theta}$, is unbiased for a parameter* θ if the expected value of $\hat{\theta}$ is θ, or expressed in notational form, $E(\hat{\theta}) = \theta$. Let $x_1, x_2, \ldots, x_n$ be a sample of n replicates from the population of method determinations.

(1) $\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$ as the *sample mean*, an unbiased estimate of the *true mean*, δ, of the determinations, the center of the distribution. For an accurate method, δ is μ, the true stack concentration.

(2) $s^2 = \frac{1}{n-1}\sum_{i=1}^{n} (x_i - \bar{x})^2$ as the *sample variance*, an unbiased estimate of the *true variance*, σ^2. This term gives a measure of the dispersion in the distribution around δ.

(3) $s = \sqrt{s^2}$ as the sample standard deviation, an alternative measure of dispersion, which estimates σ, *the true standard deviation.*

The sample standard deviation, s, however, is not unbiased for σ,[7] so a *correction factor* needs to be applied. The correction factor for a sample of size n is α_n, and the product of α_n and s is unbiased for σ. That is, $E(\alpha_n s) = \sigma$. As n increases, the value of α_n decreases, going for example from $\alpha_3 = 1.1284$, $\alpha_4 = 1.0854$ to $\alpha_{10} = 1.0281$.

We define

$$\beta = \frac{\sigma}{\delta}$$

as the *true coefficient of variation* for a given distribution. To estimate this parameter, we use a *sample coefficient of variation*, $\hat{\beta}$, defined by

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

where $\hat{\beta}$ is the ratio of the unbiased estimates of σ and δ, respectively. The coefficient of variation measures the percentage scatter in the observations about the mean and thus is a readily understandable way to express the precision of the observations.

The experimental plan for this test calls for 12 *runs*. On each run, the collaborative teams were expected to collect simultaneous samples from the stack in accordance with Method 5. Since the actual particulate emission concentration in the stack fluctuates, one can in general expect different true concentrations for each run. To permit a complete statistical analysis, the individual runs are grouped into *blocks*, where each block has approximately the same true emission concentration level.

We can apply the statistical terms of the preceding paragraphs both to the collaborators' values during a given run, and to each collaborator's values in a given block. In this report, statistical results from the first situation are referred to as *run results*. Those from the second situation are referred to as *collaborator-block results*. For example, a run mean is the average of each collaborator's concentration level for the run as obtained by Method 5. A

collaborator-block coefficient of variation is the ratio of the unbiased standard deviation to the sample mean for all the collaborator's runs grouped in the block.

The variability associated with a Method 5 concentration determination is estimated in terms of the *within-laboratory* and the *between-laboratory precision components.* In addition, a *laboratory bias component* can be estimated. The following definitions of these terms are given with respect to a *true stack concentration,* μ:

- *Within-laboratory*–The within-laboratory standard deviation, σ, measures the *dispersion in replicate single determinations* made using Method 5 by one laboratory team (same field operators, laboratory analyst, and equipment) sampling the same true concentration, μ. The value of σ is estimated from within each collaborator-block combination.

- *Between-laboratory*–The between-laboratory standard deviation, σ_b, measures the *total variability in a concentration determination* due to simultaneous Method 5 determinations by different laboratories sampling the same true stack concentration, μ. The between-laboratory variance, σ_b^2, may be expressed as

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

  and consists of a within-laboratory variance plus a *laboratory bias variance,* σ_L^2. The between-laboratory standard deviation is estimated using the run results.

- *Laboratory bias*–The laboratory bias standard deviation, $\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$, is that portion of the total variability that can be ascribed to differences in the field operators, analysts and instrumentation, and due to different manners of performance of procedural details left unspecified in the method. This term measures that part of the total variability in a determination which results from the use of the method by different laboratories, as well as from modifications in usage by a single laboratory over a period of time. The laboratory bias standard deviation is estimated from the within- and between-laboratory estimates previously obtained.

B. Collaborative Test Plan

The sampling was done through the four ports on each stack described previously, with each laboratory sampling from two ports during each run. At the end of the first hour of sampling, the teams rotated in a counterclockwise direction to the next adjacent port. The starting ports for the teams during each run were chosen through a randomization technique, and these will be shown in Table 2.

The incinerator operated only with one stack at a time. After the first week of testing, the plant shifted their operation from the Number 1 unit to the Number 2 unit. Thus, the first five samples were taken from stack Number 1, and the remaining seven from Number 2. In the absence of operating characteristics or any means of determining a true concentration level, the unit from which the determinations were made was used as the blocking factor. The resulting design, then, was two *blocks* of size 5 and 7, respectively, as shown in Table 2.

C. Collaborative Test Data

The data used in the statistical analysis of the collaborative test are presented in Table 2, along with the port at which sampling was begun. These determinations were subjected to preliminary calculation checks to ensure that all values were determined by using the proper formulas and conversion factors. The data as presented are consistent with the formulas prescribed in Method 5, and the details of the recalculation are given in Appendix B.1, along with the determinations as reported by the collaborators.

No determination was reported by Lab 104 in Run 1 due to equipment malfunction. In order to evaluate Method 5 for field testing, the analysis is done using only values which satisfy the requirements for a compliance test result. These requirements include (1) that there be a *minimum sampling volume of 60 cubic feet,* and (2) that the sample be drawn *between 90 and 110 percent of isokinetic sampling.* The values marked with

TABLE 2. PARTICULATE COLLABORATIVE TEST DATA ARRANGED IN BLOCKS, lb/scf × 10^7

Block	Run	Lab 101		Lab 102		Lab 103		Lab 104	
		Data	Port	Data	Port	Data	Port	Data	Port
1	1	219.1	A	170.6*	B	93.6	C	0.0†	D
	2	230.2	B	192.6	A	163.6	D	187.6‡	C
	3	202.7	D	207.8	A	157.8	B	380.7	C
	4	278.2	D	303.5*	A	183.6	C	82.7	B
	5	298.4	A	236.4	B	151.2	C	125.7‡	D
2	6	267.5‡	D	183.8‡	C	125.9	A	187.5	B
	7	245.4	D	171.1*‡	C	137.9	A	171.7	B
	8	468.9	D	201.4	B	179.1	A	249.0*‡	C
	9	260.0*	A	202.2*	C	157.0*	B	228.5*	D
	10	197.2	C	121.5*‡	A	123.0	B	177.3	D
	11	232.2	D	217.4*‡	B	168.5	C	229.9	A
	12	250.4	A	205.6	C	158.5	D	189.8‡	B

*Determination was made with less than 60 ft^3 of gas, corrected to standard conditions.
†No value reported for this run.
‡Determination was not obtained between 90 and 110 percent of isokinetic.

Note:
EPA policy is to express all measurements in Agency documents in metric units. When implementing this practice will result in undue cost or difficulty in clarity, NERC/RTP is providing conversion factors for the particular non-metric units used in the document. For this report, the factor is:

$$10^{-7} \text{ lb/scf} = 1.6018 \times 10^3 \ \mu g/m^3.$$

a double dagger are those with an unacceptable isokinetic variation factor, and those with an asterisk were samples of less than 60 cubic feet, corrected to standard conditions.

In these cases, the values were eliminated from the analysis, and no attempt was made to adjust these or substitute for them. While a substitution would yield a larger data base, the values would not be actual Method 5 determinations, and so could inordinately bias the results, particularly when such a large number of substitutions would be needed. This leaves a total of 32 valid determinations out of a possible 48.

Although sample ports are placed in a manner to be as nearly equivalent as possible, the unknown factors of gas flow patterns and variations can lead to a particular port showing a consistently higher or consistently lower emission concentration level over the course of the test. A test for the significance of a *port effect* is performed in Appendix B.2. Using a common rank test, no consistent tendency can be found for any of the ports to give a high or a low emission level throughout the runs. As a result of this, and the fact that two ports were sampled on each run, no port factor is included in any further analysis.

D. Precision of Method 5

There are no techniques currently available for determining the true particulate emission concentration level from a stack, and thus there is no way to determine the accuracy of the method. Further, no ancillary tests can be run to separate the analytical phase of the test from the field phase. Thus the only means available for evaluating Method 5 is to examine the precision that can be expected from a field test result.

As a preliminary to evaluating the precision of the method, the determinations are tested for *equality of variance* using Bartlett's test.[2] In addition, the determinations are passed through two common *variance stabilizing transformations*, the logarithmic and the square root, and Bartlett's test is again applied. The use of transformation

serves two purposes. First, it can put the data into an acceptable form for an analysis of variance; and second, it can provide information concerning the true nature of the distribution of the sample points.

In Appendix B.3, it is demonstrated that for the run data, the logarithmic transform provides the best fit. As has been demonstrated in a previous study by Hamil and Camann,[4] this is a strong indication of a *proportional relationship between the mean and standard deviation for the run data.*

To further this argument, a *regression line* is fit to the paired sample means and sample standard deviations for the run data in Appendix B.4. The graph in Figure B.1 shows the least squares fit to the points having been forced through the origin. The degree of fit is measured by the *coefficient of determination,* r^2, which has a value of 0.8515 for the run data. This indicates that over 85 percent of the variation in the magnitude of the standard deviation is attributed to the variation in the magnitude of the mean.

The *correlation coefficient,* $r = \sqrt{r^2}$, for the run data is 0.9228. Using tables given in Dixon and Massey,[2] this value is significant at the 5-percent level, which justifies the use of the no intercept regression line as a model for these data points.

A similar argument is presented for the collaborator-block data. For these paired values, the relationship is not as strong as it was for the run data. The value of r^2 for the least squares fit is 0.5343, which gives a value of r of 0.7309. Again referring to significance tables for r, we can determine that this value is significant at the 5-percent significance level.

The conclusion that we draw from the above results is that *there is a proportionality between the mean and the standard deviation for both the run data and the collaborator-block data.* This implies that

$$\sigma = C\delta$$

and

$$\sigma_b = C_b\delta,$$

where σ and σ_b are the within-lab and between-lab components respectively, C and C_b are constants, and δ represents the true mean determination level. This is equivalent to saying that while the standard deviations change according to the emission concentration, the ratio of the standard deviation to the mean, *the coefficient of variation, remains constant.* Thus, we may rewrite the above expressions as

$$\sigma/\delta = \beta$$

and

$$\sigma_b/\delta = \beta_b$$

where β is the *true within-laboratory coefficient of variation,* and β_b is the *true between-laboratory coefficient of variation.*

On the basis of the previous argument, then, we will estimate our precision components not directly, but by estimating the appropriate coefficients of variation and expressing the standard deviations as percentages of the mean. In Appendices B.5 and B.6, the technique for obtaining estimates of β and β_b is discussed, and it is shown that the resulting estimates are *unbiased* for the standard deviation components. Our estimates of σ and σ_b are defined with respect to the mean determination, δ.

$$\hat{\sigma} = \hat{\beta}\delta$$

and

$$\hat{\sigma}_b = \hat{\beta}_b \delta$$

The actual estimates of β and β_b are obtained in Appendix B.7 from the collaborative test data. The ***within-lab coefficient of variation,*** taken from the collaborator-block data, is $\hat{\beta} = 0.253$. Using this, we then estimate the ***within-lab standard deviation*** as

$$\hat{\sigma} = (0.253)\delta,$$

with 24 degrees of freedom.

The ***between-lab coefficient of variation,*** β_b, is estimated from the values across any particular run. From Appendix B.7, we have a value of $\hat{\beta}_b = (0.387)$, which gives an ***estimated between-lab standard deviation*** of

$$\hat{\sigma}_b = (0.387)\delta$$

at a true determination mean, δ. This estimate has 3 degrees of freedom associated with it.

From the formula presented in section A above, the ***laboratory bias standard deviation*** may be estimated as

$$\begin{aligned}\hat{\sigma}_L &= \sqrt{\hat{\sigma}_b^2 - \hat{\sigma}^2} \\ &= \sqrt{(0.387)^2\delta^2 - (0.253)^2\delta^2} \\ &= \sqrt{(0.086)\delta^2} \\ &= (0.293)\delta\end{aligned}$$

at a true determination mean, δ.

These values indicate a lack of precision in the method, especially with regard to the laboratory bias component. The differences between the labs in this study were of such a magnitude to suggest that each laboratory was obtaining a value whose usual range was essentially lab dependent. If such is the case, then there is an apparent discrepancy arising from some technique or procedure in the method which is not defined in the necessary detail. This could include the methods for sample recovery from both the filter and the probe wash, for which more detailed procedure should be specified and more care in handling should be recommended.

The within-laboratory precision could also be aided by such detail, since it could help to avoid the probable causes of unusual values, namely contamination of the probe tip by scraping against the inside of the port and loss of particulates due to probe handling and cleaning. Although not a major problem at this site, it has been a noticeable factor in a previous test.[5]

IV. COMPARISONS WITH OTHER STUDIES

Two other collaborative tests of Method 5 have been conducted,[3,5] at a cement plant and a fossil-fuel fired steam generator. The following comparisons can be made with the results of those tests.

- The within-laboratory standard deviation estimate for this study is lower than the values obtained in the other studies. The difference is due in some measure to the fact that the high value phenomenon that can effect the within-laboratory estimate is less prevalent in this test than in the other two.

- The between-laboratory standard deviation estimate for this study is comparable to that of the power plant, and lower than the value obtained from the cement plant. However, the high values obtained in the cement plant test were localized in a single laboratory's results. This caused an inflation of the laboratory bias component, which accounts for the difference between that study and the other two.

- The laboratory bias standard deviation is higher than the value obtained in the power plant test. The difference in the manner of probe cleanup and sample recovery is probably the major cause of the variability in the results from lab to lab. In this study, the infrequency of high values led to the reduction of the within-laboratory estimate, but the between-laboratory estimate remained high. This suggests that a solution to the high value problem will not, by itself, result in a great improvement in the precision demonstrated for the method but that work must be done to add the details in the technique that will enable distinct crews to perform the method in a more nearly identical manner.

V. RECOMMENDATIONS

On the basis of the conclusions and results presented and from observations by personnel in the field, the following recommendations can be made concerning Method 5:

(1) Frequency of calculation errors in the collaborative test data and differences among labs in the number of significant digits carried can be a major problem in evaluating field test results. It is recommended that a standard Method 5 computer program be written to calculate compliance test results from raw field data.

(2) More detail should be specified in the technique for sample recovery from the probe. The probe collection and handling are the probable causes of the extreme high and low values which greatly contribute to the lack of precision in the method.

(3) At present, there is no standard technique for cleaning the filter apparatus, which undoubtedly is a major contributor to the high laboratory bias. It is recommended that a detailed procedure be established and incorporated into the method.

(4) When using the method in a stack with high moisture content, filters tend to blind off rapidly, causing them to have to be changed during the course of the run. This has the effect of magnifying the handling and sample recovery requirements, thus resulting in more opportunity for errors. Sampling teams using Method 5 are encouraged to utilize as large a filter as they can accomodate when working at this type of site to minimize this problem.

APPENDIX A

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

Federal Register, Vol. 36, No. 247
December 23, 1971

2.1.4 Filter Holder—Pyrex[1] glass with heating system capable of maintaining minimum temperature of 225° F.

2.1.5 Impingers / Condenser—Four impingers connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design, modified by replacing the tip with a ½-inch ID glass tube extending to one-half inch from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip. A condenser may be used in place of the impingers provided that the moisture content of the stack gas can still be determined.

2.1.6 Metering system—Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 5° F., dry gas meter with 2% accuracy, and related equipment, or equivalent, as required to maintain an isokinetic sampling rate and to determine sample volume.

2.1.7 Barometer—To measure atmospheric pressure to ±0.1 inches Hg.

2.2 Sample recovery.

2.2.1 Probe brush—At least as long as probe.

2.2.2 Glass wash bottles—Two.

2.2.3 Glass sample storage containers.

2.2.4 Graduated cylinder—250 ml.

2.3 Analysis.

2.3.1 Glass weighing dishes.

2.3.2 Desiccator.

2.3.3 Analytical balance—To measure to ±0.1 mg.

2.3.4 Trip balance—300 g. capacity, to measure to ±0.05 g.

3. *Reagents.*

3.1 Sampling.

3.1.1 Filters—Glass fiber, MSA 1106 BH[1], or equivalent, numbered for identification and preweighed.

3.1.2 Silica gel—Indicating type, 6–16 mesh, dried at 175° C. (350° F.) for 2 hours.

3.1.3 Water.

3.1.4 Crushed ice.

3.2 Sample recovery.

3.2.1 Acetone—Reagent grade.

3.3 Analysis.

3.3.1 Water.

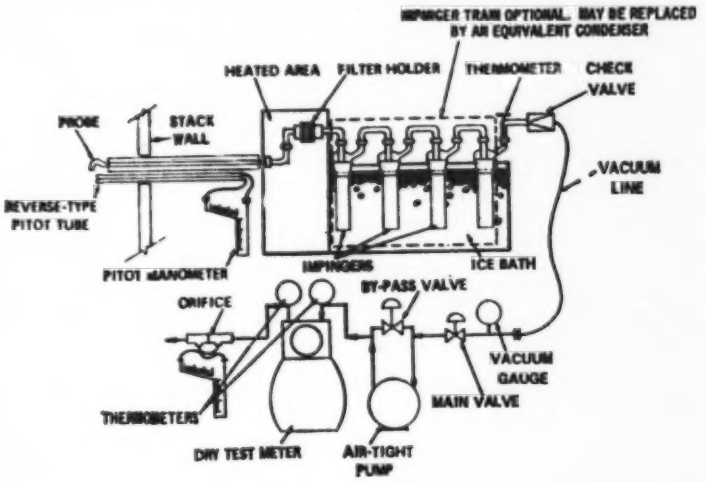


Figure 5-1. Particulate-sampling train.

3.3.2 Desiccant—Drierite,[1] indicating.

4. *Procedure.*

4.1 Sampling.

4.1.1 After selecting the sampling site and the minimum number of sampling points, determine the stack pressure, temperature, moisture, and range of velocity head.

4.1.2 Preparation of collection train. Weigh to the nearest gram approximately 200 g. of silica gel. Label a filter of proper diameter, desiccate[2] for at least 24 hours and weigh to the nearest 0.5 mg. in a room where the relative humidity is less than 50%. Place 100 ml. of water in each of the first two impingers, leave the third impinger empty, and place approximately 200 g. of preweighed silica gel in the fourth impinger. Set up the train without the probe as in Figure 5-1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 15 in. Hg vacuum. A leakage rate not in excess of 0.02 c.f.m. at a vacuum of 15 in. Hg is acceptable. Attach the probe and adjust the heater to provide a gas temperature of about 250° F. at the probe outlet. Turn on the filter heating system. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger as low as possible and preferably at 70° F., or less. Temperatures above 70° F. may result in damage to the dry gas meter from either moisture condensation or excessive heat.

4.1.3 Particulate train operation. For each run, record the data required on the example sheet shown in Figure 5-2. Take readings at each sampling point, at least every 5 minutes, and when significant changes in stack conditions necessitate additional adjustments in flow rate. To begin sampling, position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Sample for at least 5 minutes at each traverse point; sampling time must be the same for each point. Maintain isokinetic sampling throughout the sampling period. Nomographs are available which aid in the rapid adjustment of the sampling rate without other computations. APTD-0576 details the procedure for using these nomographs. Turn off the pump at the conclusion of each run and record the final readings. Remove the probe and nozzle from the stack and handle in accordance with the sample recovery process described in section 4.2.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and applicability.*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and its weight is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources only when specified by the test procedures for determining compliance with New Source Performance Standards.

2. *Apparatus.*

2.1 Sampling train. The design specifications of the particulate sampling train used by EPA (Figure 5-1) are described in APTD-0581. Commercial models of this train are available.

2.1.1 Nozzle—Stainless steel (316) with sharp, tapered leading edge.

2.1.2 Probe—Pyrex[1] glass with a heating system capable of maintaining a minimum gas temperature of 250° F. at the exit end during sampling to prevent condensation from occurring. When length limitations (greater than about 8 ft.) are encountered at temperatures less than 600° F., Incoloy 825[1], or equivalent, may be used. Probes for sampling gas streams at temperatures in excess of 600° F. must have been approved by the Administrator.

2.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.

[1] Trade name.

[1] Trade name.

[2] Dry using Drierite[1] at 70° F. ± 10° F.

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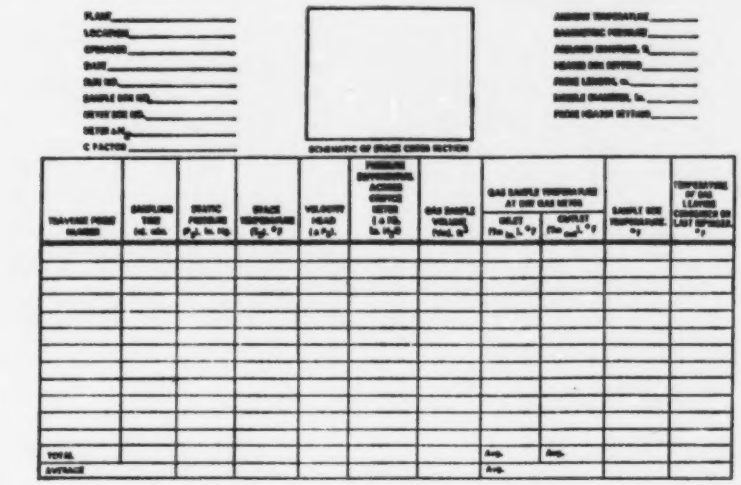

Figure 5-2. Particulate field data.

4.2 Sample recovery. Exercise care in moving the collection train from the test site to the sample recovery area to minimize the loss of collected sample or the gain of extraneous particulate matter. Set aside a portion of the acetone used in the sample recovery as a blank for analysis. Measure the volume of water from the first three impingers, then discard. Place the samples in containers as follows:

Container No. 1. Remove the filter from its holder, place in this container, and seal.

Container No. 2. Place loose particulate matter and acetone washings from all sample-exposed surfaces prior to the filter in this container and seal. Use a razor blade, brush, or rubber policeman to lose adhering particles.

Container No. 3. Transfer the silica gel from the fourth impinger to the original container and seal. Use a rubber policeman as an aid in removing silica gel from the impinger.

4.3 Analysis. Record the data required on the example sheet shown in Figure 5-3. Handle each sample container as follows:

Container No. 1. Transfer the filter and any loose particulate matter from the sample container to a tared glass weighing dish, desiccate, and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 2. Transfer the acetone washings to a tared beaker and evaporate to dryness at ambient temperature and pressure. Desiccate and dry to a constant weight. Report results to the nearest 0.5 mg.

Container No. 3. Weigh the spent silica gel and report to the nearest gram.

5. *Calibration.*

Use methods and equipment which have been approved by the Administrator to calibrate the orifice meter, pitot tube, dry gas meter, and probe heater. Recalibrate after each test series.

6. *Calculations.*

6.1 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 5-2).

6.2 Dry gas volume. Correct the sample volume measured by the dry gas meter to standard conditions (70° F., 29.92 inches Hg) by using Equation 5-1.

$$V_{m_{std}} = V_m\left(\frac{T_{std}}{T_m}\right)\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{P_{std}}\right) = \left(17.71\ \frac{°R}{in.\ Hg}\right)V_m\left(\frac{P_{bar}+\frac{\Delta H}{13.6}}{T_m}\right)$$

equation 5-1

where:

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

V_m = Volume of gas sample through the dry gas meter (meter conditions), cu. ft.

T_{std} = Absolute temperature at standard conditions, 530° R.

T_m = Average dry gas meter temperature, °R.

P_{bar} = Barometric pressure at the orifice meter, inches Hg.

ΔH = Average pressure drop across the orifice meter, inches H_2O.

13.6 = Specific gravity of mercury.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.3 Volume of water vapor.

$$V_{w_{std}} = V_{l_c}\left(\frac{\rho_{H_2O}}{M_{H_2O}}\right)\left(\frac{RT_{std}}{P_{std}}\right) = \left(0.0474\ \frac{cu.\ ft.}{ml.}\right)V_{l_c}$$

equation 5-2

where:

$V_{w_{std}}$ = Volume of water vapor in the gas sample (standard conditions), cu. ft.

V_{l_c} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

ρ_{H_2O} = Density of water, 1 g./ml.

M_{H_2O} = Molecular weight of water, 18 lb./lb.-mole.

R = Ideal gas constant, 21.83 inches Hg—cu. ft./lb.-mole-°R.

T_{std} = Absolute temperature at standard conditions, 530° R.

P_{std} = Absolute pressure at standard conditions, 29.92 inches Hg.

6.4 Moisture content.

$$B_{ws} = \frac{V_{w_{std}}}{V_{m_{std}} + V_{w_{std}}}$$

equation 5-3

where:

B_{ws} = Proportion by volume of water vapor in the gas stream, dimensionless.

$V_{w_{std}}$ = Volume of water in the gas sample (standard conditions), cu. ft.

$V_{m_{std}}$ = Volume of gas sample through the dry gas meter (standard conditions), cu. ft.

6.5 Total particulate weight. Determine the total particulate catch from the sum of the weights on the analysis data sheet (Figure 5-3).

6.6 Concentration.

6.6.1 Concentration in gr./s.c.f.

$$c'_s = \left(0.0154\frac{gr.}{mg.}\right)\left(\frac{M_n}{V_{m_{std}}}\right)$$

equation 5-4

where:

c'_s = Concentration of particulate matter in stack gas, gr./s.c.f., dry basis.

M_n = Total amount of particulate matter collected, mg.

$V_{m_{std}}$ = Volume of gas sample through dry gas meter (standard conditions), cu. ft.

APPENDIX B

STATISTICAL METHODS

STATISTICAL METHODS

This appendix consists of various sections which contain detailed statistical procedures carried out in the analysis of the particulate matter collaborative study data. Reference to these sections has been made at various junctures in the Statistical Design and Analysis part of the body of this report. Each Appendix B section is an independent ad hoc statistical analysis pertinent to a particular problem addressed in the body of the report.

B.1 Preliminary Analysis of the Original Collaborative Test Data

Preliminary recalculations were made on the originally reported data to ensure that the proper formulas were used and that the concentrations used in the analysis were correctly computed. There is some question about the propriety of this in light of the philosophy of collaborative testing expressed previously. However, no computation is made that is not the direct result of the actual data obtained by the collaborator. Recalculation only ensures that there is some consistency to the number of significant digits carried and that the concentration used in the analysis does not contain a calculation error that will bias the results. The data originally reported are shown in Table B.1, and comparison with Table 2 in Section III indicates the need for such a step.

TABLE B.1. ORIGINAL PARTICULATE CONCENTRATIONS, lb/scf $\times 10^7$

Run	Collaborator			
	Lab 101	Lab 102	Lab 103	Lab 104
1	219.0	170.9	93.6	Missing
2	230.0	192.6	163.6	187.6
3	203.0	208.0	157.8	380.7
4	278.0	303.0	183.7	82.7
5	298.0	236.0	153.2	125.6
6	268.0	183.8	125.9	187.5
7	245.0	171.1	137.9	171.7
8	469.0	201.5	179.1	249.0
9	260.0	202.0	157.0	228.5
10	197.0	121.5	123.0	177.3
11	232.0	217.4	168.5	229.9
12	251.0	205.6	158.5	189.8

Each collaborator reported a concentration for all runs, with the exception of Lab 104 in Run 1. This resulted from a malfunction in the temperature indicator which caused the collaborator to be unable to complete the run. In numerous other cases, however, the determinations were unacceptable with respect to the requirements listed in the *Federal Register*,[1] a minimum sampling volume of 60 standard cubic feet and an isokinetic factor of 90 to 110 percent. The end result was that of the 47 total determinations made, only 32 conformed to the definition of a replication for a compliance test, and only these were used in the analysis.

Since there is no technique available for determining the true particulate emission concentration, the procedure for grouping the runs into fairly *homogeneous blocks* is somewhat arbitrary. The only readily available means for establishing blocks was to divide the runs according to the two weeks during which the test was conducted. The assumption that is made under these circumstances is that there is an essentially constant level of particulate emissions over each week's operation. This assumption may not be valid due to the variety of materials burned and normal fluctuations; however, a preliminary statistical test indicated no reason to believe there were large differences in the true emission level during the two weeks of testing. Therefore, this blocking scheme was accepted as suitable.

There were several values in the collaborators' data that seemed inconsistent with the remainder of the data. These included the low values of Lab 103 in Run 1 and Lab 104 in Run 4, and the high values of Lab 104 in Run 3 and Lab 101 in Run 8. The presence of these high and low values is a consistent problem with the use of Method 5. There has been some discussion of the possible causes of these occurrences, with careless probe handling and probe contamination being the most likely candidates. There is not sufficient cause to eliminate these from the analysis as outlying values, however, since their presence is apparently characteristic of the type of results one can expect from the method in field testing.

B.2 Significance of the Port Effect

The test was designed to offset and eliminate any effect of the possible differences in observed concentration levels resulting from the pattern of gas flow in the stack. The possibility does exist, however, that a particular port will consistently show a higher or lower value than the others.

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A non-parametric analysis of variance is used to test the *hypothesis of no port effect*. The test is that of Kruskal-Wallis,[2] and the resulting statistic is given by

$$H = \frac{12}{N(N+1)} \sum_{i=1}^{k} \frac{Ri^2}{n_i} - 3(N+1)$$

where

R_i–the sum of the ranks of the observations from the i^{th} port

n_i–the number of valid determinations made from the i^{th} port

$N = \sum_{i=1}^{k} n_i$–the total number of valid determinations from the test

and

k–the number of ports.

The usable data points are presented in Table B.2, by port, along with the rank of each value. The values are assigned rankings in the collective sample, with the highest determination in each week given rank 1. The sum of the ranks for each port and the number of determinations are shown at the bottom of each column. Separate tests are performed for the four ports from the first stack and for the four from the second stack.

TABLE B.2. SIGNIFICANCE OF PORT EFFECT

Block		Port							
		A		B		C		D	
1		219.1	(6)*	230.2	(5)	93.6	(14)	163.6	(11)
		192.6	(9)	157.8	(12)	380.7	(1)	202.7	(8)
		207.8	(7)	82.7	(15)	183.6	(10)	278.2	(3)
		298.4	(2)	236.4	(4)	151.2	(13)		
	R_i		24		36		38		22
	n_i		4		4		4		3
$H = 1.5167$									
2		125.9	(16)	187.5	(9)	197.2	(8)	245.4	(3)
		137.9	(15)	171.7	(12)	168.5	(13)	468.9	(1)
		179.1	(10)	201.4	(7)	205.6	(6)	177.3	(11)
		229.9	(5)	123.0	(17)			232.2	(4)
		250.4	(2)					158.5	(14)
	R_i		48		45		27		33
	n_i		5		4		3		5
$H = 1.9941$									

*Number in parentheses is rank of value in combined sample.

For the first week's test, the value of H was 1.517, while for the second week, H had a value of 1.994. For a value of H to be significant, it must exceed a value taken from a table of the chi-square distribution with $k - 1 = 4 - 1 = 3$ degrees of freedom. The tabled value at a 5-percent level of significance is 7.81. Thus, the difference between the determinations due to a port effect is essentially nonexistent, and on this basis, the port factor is eliminated from further analysis.

B.3 Transformations

In order to gain information concerning the distributional nature of the Method 5 determinations, the observations are passed through two common *variance stabilizing transformations*, the *logarithmic* and the *square root*. To determine the adequacy of the transformations, Bartlett's test for homogeneity of variance[2] is used to measure the degree of equality achieved.

The results of the test are shown in Table B.3 for the two transformations, as well as for the data in their original form (linear). Bartlett's test statistic is presented along with degrees of freedom and the associated *significance level* for each transformation. The significance levels are obtained from a chi-square distribution with the degrees of freedom shown.

TABLE B.3. DATA TRANSFORMATION TO ACHIEVE RUN EQUALITY OF VARIANCE

Transformation	Test Statistic	Degrees of Freedom	Significance
Linear	8.678	10	0.56
Logarithmic	5.923	10	0.82
Square Root	6.505	10	0.77

Clearly, at any usual significance level, all three forms of the data provide an acceptable model from the equality of variance aspect. However, the highest degree of equality is obtained through the logarithmic transformation, and this is taken to be the appropriate model.

In a previous study by Hamil and Camann,[4] this has been shown to be an indication that there is a *proportionality between the mean and standard deviation* for the run data. This same model has been shown to be appropriate for data from particulate matter emissions in a study at a powerplant as well.[5]

B.4 Empirical Relationship Between Mean and Standard Deviation

In Appendix B.3, an underlying proportionality between the mean and standard deviation for the run data is indicated. In this section, we will attempt to establish this relationship empirically from the determinations obtained at the Holmes Road Incinerator study. Let

x_{ijk} be the concentration reported during run k in block j by lab i

$\bar{x}_{.jk} = \frac{1}{p}\sum_{i=1}^{p} x_{ijk}$ be the mean for run k, block j across collaborators, for p collaborators

$s_{jk} = \sqrt{\frac{1}{p-1}\sum_{i=1}^{p}(x_{ijk} - \bar{x}_{.jk})^2}$ be the run standard deviation

Table B.4 gives the values of the sample statistics obtained at the Holmes Road site. There is a general tendency for the standard deviation in the run data to rise as the mean level of concentration rises. To further this idea, the paired statistics are plotted, and a *least squares regression line* is fit to the points. The model used is the *no intercept model*, or a line forced through the origin, since a mean of zero could only occur in the event that each determination equalled zero. The model used, then, is

$$s_{jk} = b\,\bar{x}_{.jk}$$

where b is a constant. The individual points and the regression line thus obtained are shown in Figure B.1. The measure of the degree of fit obtained is the *coefficient of determination*, r^2, which for the no intercept model is obtained by the formula[6]

TABLE B.4. INTERLABORATORY RUN SUMMARY

Block	Run	Mean Particulate Concentration, lb/scf	Std. Dev., lb/scf
1	1	156.3	88.7
	2	195.5	33.4
	3	237.2	98.2
	4	181.5	97.8
	5	228.7	73.9
2	6	156.7	43.6
	7	185.0	55.0
	8	283.1	161.3
	9*	0.0	0.0
	10	165.8	38.4
	11	210.2	36.1
	12	204.8	46.0

*No usable results in Sample 9.

$$r^2 = \frac{\left(\sum_{i=1}^{n} x_i y_i\right)^2}{\sum_{i=1}^{n} x_i^2 \sum_{i=1}^{n} y_i^2} = \frac{\left(\sum_{i=1}^{n} \bar{x}_{.jk}\, s_{jk}\right)^2}{\sum_{i=1}^{n} \bar{x}_{.jk}^2 \sum_{i=1}^{n} s_{jk}^2}$$

For the run data, the value of r^2 is 0.8515, indicating that approximately 85 percent of the variation in the magnitude of the standard deviation is attributed to variation in the magnitude of the mean. The *correlation coefficient*, $r = \sqrt{r^2}$, between $\bar{x}_{.jk}$ and s_{jk} is 0.9228. From a table of significant values of r presented in Dixon and Massey,[2] this value indicates that a ***significant amount of correlation exists*** between the sample mean and sample standard deviation for the no intercept model used.

A similar analysis can be used on the collaborator-block values. If we let n_{ij} be the number of valid determinations in block j by collaborator i, then we have

$$\bar{x}_{ij.} = \frac{1}{n_{ij}} \sum_{k=1}^{n_{ij}} x_{ijk} \quad \text{as the mean for collaborator } i \text{ in block } j$$

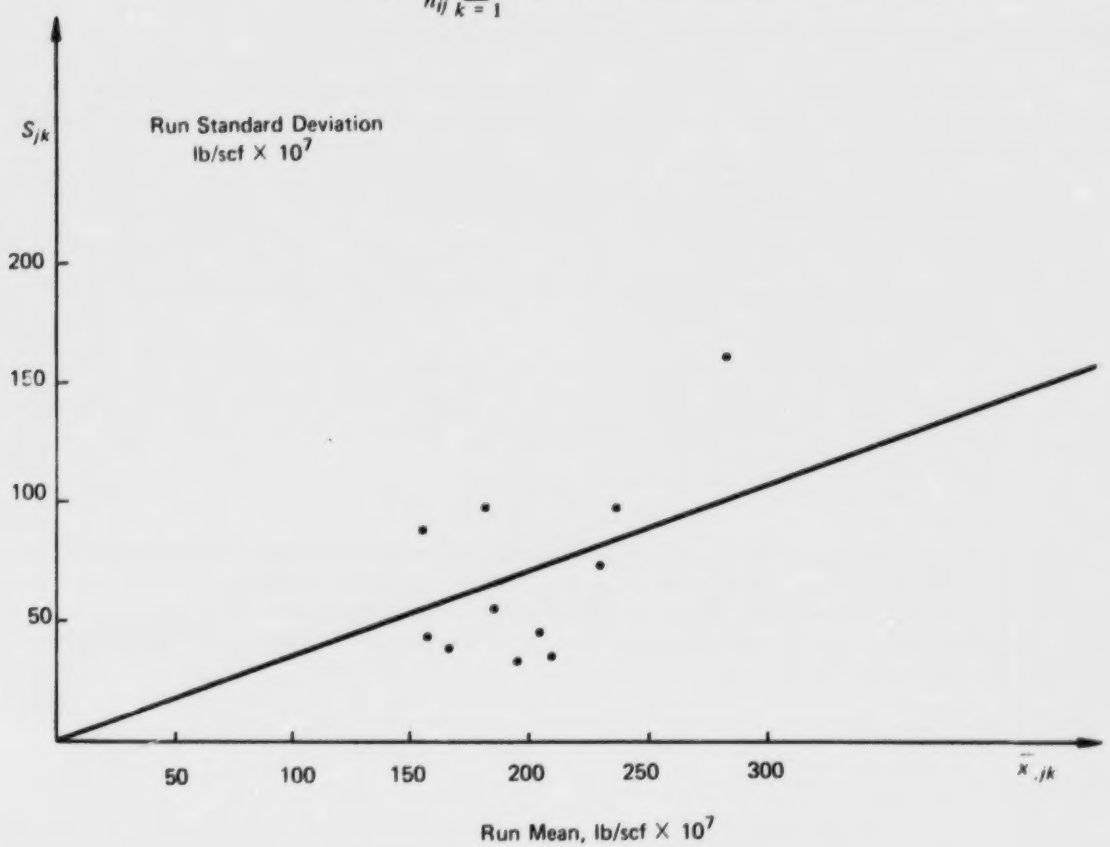

FIGURE B.1. INTERLABORATORY RUN PLOT

and

$$s_{ij} = \sqrt{\frac{1}{n_{ij} - 1} \sum_{k=1}^{n_{ij}} (x_{ijk} - \bar{x}_{ij.})^2}$$ as the collaborator-block standard deviation.

TABLE B.5. INTRALABORATORY COLLABORATOR BLOCK SUMMARY

Block	Collaborator	Mean Particulate Concentration, lb/scf	Std. Dev., lb/scf
1	Lab 101	245.7	40.7
	Lab 102	212.3	22.2
	Lab 103	150.0	33.8
	Lab 104	231.7	210.7
2	Lab 101	278.8	108.3
	Lab 102	203.5	3.0
	Lab 103	148.8	23.3
	Lab 104	191.6	26.4

The eight pairs of values obtained are shown in Table B.5. As before, we fit a regression line through the origin to these points and try to determine the adequacy of the fit. For the collaborator-block data, the value of r^2 is found to be 0.5343. It is apparent from Figure B.2 that the degree of fit is not as strong as for the run data.

The value of r is 0.7309, which is, however, still above the critical value in the table, at the 0.05 level. Thus, we can still say that there is evidence of a *proportional relationship*. This, coupled with the results of the previous study, gives credence to the use of this as a model for the data.

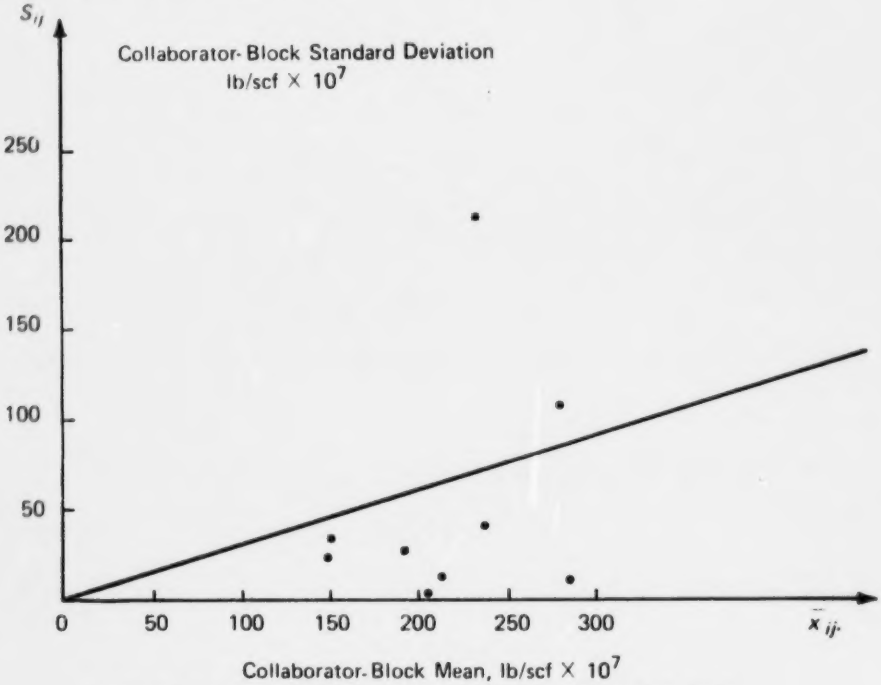

FIGURE B.2. INTRALABORATORY COLLABORATOR-BLOCK PLOT

B.5 Unbiased Estimation of Standard Deviation Components

In Appendix B.4, an investigation into the correlation between the mean and standard deviation for the collaborator-block data revealed that there was an empirical basis for accepting the model for the *within-lab standard deviation* of

$$\sigma = \beta\delta$$

for the data. To estimate this standard deviation, we use the relationship

$$s_{ij} = C\bar{x}_{ij.}$$

where C is a constant, representing the proportionality. As previously discussed, s_{ij} is a biased estimator for the true standard deviation, σ. The correction factor for removing the bias is dependent on the sample size n, and is given by Ziegler[7] as

$$\alpha_n = \sqrt{\frac{2}{3}} \frac{\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right)},$$

where Γ represents the standard gamma function. Thus, we can say that

$$E(\alpha_n s_{ij}) = \sigma$$

or

$$\begin{aligned} \sigma &= \alpha_n E(s_{ij}) \\ &= \alpha_n E(C\bar{x}_{ij.}) \\ &= \alpha_n C E(\bar{x}_{ij.}) \\ &= \alpha_n C \delta \\ &= \beta\delta. \end{aligned}$$

so that in obtaining an unbiased estimate of β, we can obtain an unbiased estimate of σ as well. Thus, we *define an estimator* for σ, $\hat{\sigma}$, where

$$\hat{\sigma} = \hat{\beta}\delta.$$

From Appendices B.3 and B.4, we determine that a suitable model for the run data is given by

$$\sigma_b = \beta_b \delta$$

where $\sigma_b = \sqrt{\sigma_L^2 + \sigma^2}$ is the *between-lab standard deviation.* Empirically, we have

$$s_{jk} = C_b \bar{x}_{.jk}$$

and s_{jk} is a biased estimator for σ_b. Thus, for p collaborators,

$$E(\alpha_p s_{jk}) = \sigma$$

and we have

$$\begin{aligned} \sigma &= E(\alpha_p s_{jk}) \\ &= \alpha_p E(C_b \bar{x}_{.jk}) \\ &= \alpha_p C_b E(\bar{x}_{.jk}) \\ &= \alpha_p C_b \delta \\ &= \beta_b \delta. \end{aligned}$$

Obtaining an estimate of β_b, we have a *new estimator*, $\hat{\sigma}_b$, of σ_b given by

$$\hat{\sigma}_b = \hat{\beta}_b \delta .$$

But $\sigma_b = \sqrt{\sigma_L^2 + \sigma^2}$ implies

$$\sigma_b^2 = \sigma_L^2 + \sigma^2$$

$$\sigma_L^2 = \sigma_b^2 - \sigma^2$$

$$\sigma_L = \sqrt{\sigma_b^2 - \sigma^2}$$

and substituting our estimates of σ_b and σ, we have

$$\sigma_L = \sqrt{\hat{\beta}_b^2 \delta^2 - \hat{\beta}^2 \delta^2}$$

$$= \sqrt{\hat{\beta}_b^2 - \hat{\beta}^2}\ \delta .$$

so that the *laboratory bias standard deviation* may be estimated as a percentage of the mean as well.

B.6 Weighted Coefficient of Variation Estimates

The technique used for obtaining estimates of the coefficients of variation of interest is to use a linear combination of the individual beta values obtained. The linear combination used will be of the form

$$\frac{1}{k} \sum_{j=1}^{k} w_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is the jth coefficient of variation estimate, k is the total number of estimates, and w_j is a weight applied to the jth estimate.

As previously discussed, the individual estimate of β is obtained as

$$\hat{\beta} = \frac{\alpha_n s}{\bar{x}}$$

for a sample of size n. This estimator is shown in B.5 to be unbiased for the true coefficient of variation. However, since we are dealing with small samples to obtain our individual estimates, weighting is more desirable in that it provides for more contribution from those values derived from larger samples. There is more variability in the beta values obtained from the smaller samples, as can be seen by inspecting the variance of the estimator. We have that

$$\mathrm{Var}(\hat{\beta}) = \mathrm{Var}\left(\frac{\alpha_n s}{\bar{x}}\right)$$

$$= \alpha_n^2\ \mathrm{Var}\left(\frac{s}{\bar{x}}\right)$$

$$= \alpha_n^2 \left[\frac{\beta^2}{2n}(1 + 2\beta^2)\right]$$

for normally distributed samples,[8] and true coefficient of variation, β. Rewriting this expression, we have

$$\mathrm{Var}(\hat{\beta}) = \frac{\alpha_n^2}{n}\left[\frac{\beta^2}{2}(1+2\beta^2)\right]$$

and all terms are constant except for α_n^2 and n. Thus, the magnitude of the variance changes with respect to the factor α_n^2/n. Now, since α_n decreases as n increases, the factor α_n^2/n must decrease as n increases, and the variance is reduced.

The weights, w_j, are determined according to the technique used in weighted least squares analysis[6], which gives a minimum variance estimate of the parameter. The individual weight, w_i, is computed as the inverse of the variance of the estimate, $\hat{\beta}_i$, and then standardized. Weights are said to be standardized when

$$\frac{1}{k}\sum_{j=1}^{k} w_j = 1$$

To standardize, the weights are divided by the average of the inverse variances for all the estimates. Thus, we can write

$$w_i = \frac{u_i}{\bar{u}}$$

where

$$u_i = \frac{1}{\mathrm{Var}(\hat{\beta}_i)}$$

and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k}\frac{1}{\mathrm{Var}(\hat{\beta}_j)}$$

Now, from the above expressions we can determine u_i, $\bar{u}$ and w_i for the beta estimates. For any estimate, β_i,

$$u_i = \frac{1}{\mathrm{Var}(\beta_i)}$$

$$= \frac{n_i}{\alpha_{n_i}^2}\left[\frac{2}{\beta^2(1+2\beta^2)}\right]$$

for sample size n_i, and

$$\bar{u} = \frac{1}{k}\sum_{j=1}^{k}\frac{1}{\mathrm{Var}(\beta_j)}$$

$$= \frac{1}{k}\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\left[\frac{2}{\beta^2(1+2\beta^2)}\right]$$

$$= \frac{1}{k}\left[\frac{2}{\beta^2(1+2\beta^2)}\right]\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}$$

Thus, the ith weight, w_i, is

$$w_i = \frac{u_i}{\bar{u}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}\left[\dfrac{2}{\beta^2(1+2\beta^2)}\right]}{\dfrac{1}{k}\left[\dfrac{2}{\beta^2(1+2\beta^2)}\right]\sum\dfrac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{n_i}{\alpha_{n_i}^2}}{\dfrac{1}{k}\displaystyle\sum_{i=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}$$

$$= \frac{\dfrac{k_{n_i}}{\alpha_{n_i}^2}}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}} .$$

The estimated coefficient of variation is

$$\hat{\beta} = \frac{1}{k}\sum_{j=1}^{k} w_j\hat{\beta}_j$$

$$= \frac{1}{k}\sum_{i=1}^{k}\frac{k_{n_i}\alpha_{n_i}^2}{\displaystyle\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}}\hat{\beta}_i$$

$$= \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i}{\alpha_{n_i}^2}\cdot\frac{\alpha_{n_i}s}{\bar{x}}$$

$$= \left[\sum_{j=1}^{k}\frac{n_j}{\alpha_{n_j}^2}\right]^{-1}\sum_{i=1}^{k}\frac{n_i s}{\alpha_{n_i}\bar{x}} .$$

B.7 Estimation of Precision Components

In Appendices B.3 and B.4, the relationships are established for the within-laboratory standard deviation, σ, and the between-laboratory standard deviation, σ_b,

$$\sigma = \beta\delta$$

and

$$\sigma_b = \beta_b\delta$$

where δ is the true mean of the determinations. In Appendix B.5, it is shown that for the laboratory bias standard deviation, σ_L, the above expressions imply

$$\sigma_L = \beta_L \delta$$

$$= (\sqrt{\beta_b^2 - \beta^2})\delta .$$

In Appendix B.6, the technique for obtaining an estimate of a coefficient of variation as a linear combination of the individual values is discussed. The estimator is of the form

$$\hat{\beta} = \frac{1}{k} \sum_{j=1}^{k} w_j \hat{\beta}_j$$

where $\hat{\beta}_j$ is the estimated beta from the jth sample, w_j is the weight given to that estimate, and k is the number of estimates obtained. For the run data, this becomes

$$\hat{\beta}_b = \frac{1}{11} \sum_{j=1}^{12} w_j \hat{\beta}_j .$$

The factor 11 is used since one run had no usable determinations. In Table B.6, the individual coefficients of variation and their corresponding weights are given. Using these in the above equation, we obtain

TABLE B.6. RUN BETA ESTIMATES AND WEIGHTS

Run	Beta Hat	Weight
1	0.7114	0.565
2	0.1928	1.045
3	0.4494	1.507
4	0.6078	1.045
5	0.3647	1.045
6	0.3484	0.565
7	0.3353	1.045
8	0.6427	1.045
9*	0.0000	0.000
10	0.2613	1.045
11	0.1940	1.045
12	0.2532	1.045

*No usable determinations in this run.

$$\hat{\beta}_b = (0.387)$$

and consequently

$$\hat{\sigma}_b = (\hat{\beta}_b \delta)$$

$$= (0.387)\delta$$

This estimate has $4 - 1 = 3$ degrees of freedom for comparison of four laboratories.

Similarly, for the within-laboratory coefficient of variation we have

$$\hat{\beta} = \frac{1}{8} \sum_{j=1}^{8} w_j \hat{\beta}_j ,$$

for the 8 collaborator-block combinations. The individual estimates and their weights are shown in Table B.7. Substituting, we have

TABLE B.7. COLLABORATOR-BLOCK BETA ESTIMATES AND WEIGHTS

Block	Collaborator	Beta Hat	Weight
1	Lab 101	0.1763	1.310
	Lab 102	0.1182	0.698
	Lab 103	0.2394	1.310
	Lab 104	1.1398	0.377
2	Lab 101	0.4131	1.310
	Lab 102	0.0183	0.377
	Lab 103	0.1644	1.611
	Lab 104	0.1493	1.007

$$\hat{\beta} = (0.253)$$

and an estimated standard deviation of

$$\hat{\sigma} = \hat{\beta}\delta$$

$$= (0.253)\delta .$$

This estimate has $32 - 8 = 24$ degrees of freedom, for the 32 determinations divided into 8 collaborator-block combinations.

Using these values in the equation for the laboratory bias coefficient of variation, we estimate

$$\hat{\beta}_L = [\sqrt{(0.387)^2 - (0.253)^2}]$$

$$= \sqrt{0.086}$$

$$= 0.293,$$

and thus, the estimated laboratory bias standard deviation is

$$\hat{\sigma}_L = \hat{\beta}_L \delta$$

$$= (0.293)\delta.$$

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